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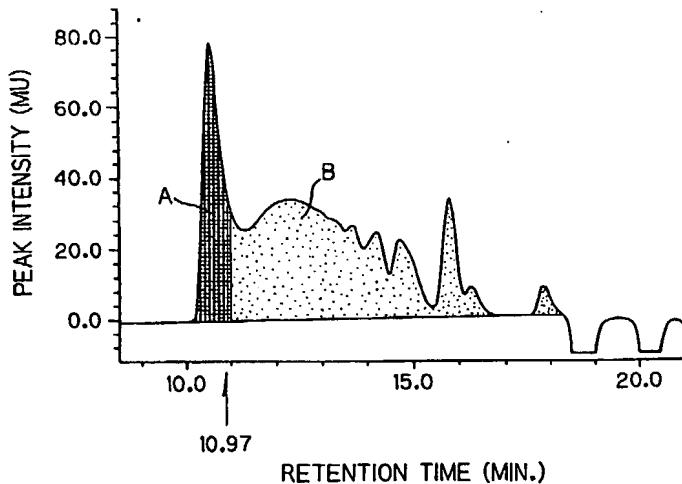
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(54) Rubber.

(57) A rubber composition having compatibly high elasticity and high breaking resistance comprises a rubber, a novolac resin having a softening point of 90 - 150 °C prepared by copolycondensation of xylene (A) and phenols (B), A/B = 25/75 - 75/25, by using an aldehyde, and a compound capable of donating methylene group when heated.

## FIG. 1



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BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a rubber composition, and more particularly, to a rubber composition having compatibly high elasticity and high breaking resistance.

Description of the Related Art

10 Rubber products used under dynamic using conditions such as tires and the like are deteriorated by environmental deterioration such as heat, oxygen, light and the like and further by mechanical fatigue, and finally broken resulting in the end of life.

In particular, steel cord coating rubber compositions are suffering from thermal oxidative deterioration as well as mechanical repeating fatigue, and thereby there occurs an accident, so-called belt edge separation, and the product life is shortened.

15 In order to prevent such deterioration and breaking, it is necessary to prevent the thermal oxidative deterioration and decrease the amount of deformation of rubber products caused by external force. For the purpose of attaining such purposes, it is effective to enhance the elasticity of the rubber compositions constituting such products.

20 Heretofore, there are known various methods for making rubber compositions highly elastic, for example, increasing the amount of carbon black to be added, or increasing the amount of a vulcanizing agent such as sulfur or a vulcanization accelerator to enhance the network density.

Indeed, those methods can impart a high elasticity to rubber compositions, but deteriorate breaking resistance represented by elongation at break, and in addition, in the carbon black increasing method the 25 heat generation property is degraded and the workability is lowered due to the increase in viscosity when non-vulcanized while in the sulfur increasing method, resistance to thermal oxidative deterioration is lowered and the life of the rubber products is rather shortened.

Further, there is known a method of enhancing the elasticity by using both resorcin or phenolic resin 30 and a methylene group donor. In particular, in the case of steel cord coating rubber compositions, there are disclosed improvements in adhesion between steel cord and rubber in Japanese Patent Publication No. 4582/1988, Japanese Patent Application Laid-open No. 160331/1983, Japanese Patent Publication No. 4332/1980 and the like, but these aim at good adhesion between steel cord and rubber only, and it is not contemplated to make high elasticity and breaking resistance of rubber compositions compatible, and therefore, the compatibility is not sufficiently improved.

35 Heretofore, there have been known copolycondensed resins derived from different phenols such as a copolycondensed resin of xylenol, p-t-octylphenol and formaldehyde, but such copolycondensed resins are not effective for improving the characteristics, that is, high elasticity and breaking resistance of rubber compositions as contemplated by the present invention.

That is, it has been very difficult to render high elasticity and breaking resistance compatible and this 40 difficulty has been a big problem in improving resistance of rubber compositions to external force.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a rubber composition having a compatibility of high 45 elasticity and high breaking resistance.

Another object of the present invention is to provide a rubber composition exhibiting a compatibility of high elasticity and high breaking resistance and further an improved heat generation property.

According to the present invention, there is provided a rubber composition which comprises 100 parts 50 by weight of a rubber selected from the group consisting of natural rubber, synthetic rubber and a mixture thereof, 0.5 - 10 parts by weight of a novolac resin having a softening point of 90 - 150 °C prepared by the copolycondensation of xylenol (A) and a phenol (B) selected from the group consisting phenol, cresol and a mixture thereof at a molar ratio (A/B) ranging from 25/75 to 75/25, by using an aldehyde compound, and 0.5 - 10 parts by weight of a compound capable of donating a methylene group when heated.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a GPC (gel permeation chromatograph) chart showing a proportion of the high molecular weight component in the copolycondensed resin according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The rubber composition of the present invention is different from compositions obtained from conventional carbon black increasing methods and sulfur increasing methods, and can attain a high compatibility between high elasticity and breaking resistance which could not be attained by conventional methods using resorcin and phenolic resin.

The rubber used in the present invention may be optionally selected from natural rubber, synthetic rubbers and blend rubbers. Exemplary suitable synthetic rubbers include synthetic polyisoprene rubber, styrene-butadiene copolymer rubber, polybutadiene rubber, butyl rubber, and halogenated butyl rubber, but are not limited thereto.

The copolycondensed novolac resin used in the present invention may be prepared by copolycondensing xyleneol as component (A), preferably 3,5-xyleneol and a phenol as component (B) such as phenol, cresol and the like, preferably phenol, at a molar ratio (A/B) of 25/75 - 75/25, preferably 40/60 - 60/40, by using an aldehyde compound.

As is clear from above, the copolycondensed novolac resin is formed by chemically bonding the three components, xyleneol (A), a phenol (B) and an aldehyde compound together. Therefore, for example, a simple blend of a xyleneol-aldehyde resin and a phenol-aldehyde resin is not the copolycondensed novolac resin of the present invention.

The aldehyde compound may be formaldehyde, acetaldehyde, benzaldehyde, salicylaldehyde, acrolein and the like. Formaldehyde is preferable from an industrial point of view since it is economical and safe.

The copolycondensed novolac resin may be prepared, for example, by (i) reacting an aldehyde compound with a mixture of xyleneol (A) and a phenol (B), (ii) reacting a reaction product of xyleneol (A) and an aldehyde compound with a reaction product of a phenol (B) and an aldehyde compound, (iii) reacting xyleneol (A) with a reaction product of a phenol (B) and an aldehyde compound, or (iv) reacting a phenol (B) with a reaction product of xyleneol (A) and an aldehyde compound.

When the molar ratio (A/B) of this copolycondensed resin is less than 25/75, that is, the amount of xyleneol is much less than that of a phenol, the modulus of elasticity as well as the breaking resistance is lowered.

When the molar ratio (A/B) is larger than 75/25, that is, the amount of xyleneol is much larger than that of a phenol, the curing reaction proceeds slowly so that a further increase in elasticity can not be attained, and moreover, the uncured resin remains in the rubber composition so that the heat generation property of the resulting rubber composition is deteriorated.

The softening point of the resin is 90 - 150 °C in the present invention. When the softening point is lower than 90 °C, the modulus of elasticity is lowered and moreover, there occurs blocking phenomenon during storing the resin.

On the contrary, when the softening point is higher than 150 °C, the dispersion in the rubber can not be effected suitably resulting in the lowering of modulus of elasticity and deterioration of the heat generation property.

In order to improve the heat generation property of the rubber composition, in a molecular weight distribution, the copolycondensed novolac resin preferably contains a high molecular weight component having a molecular weight in terms of polystyrene of 5200 or more in an amount corresponding to a peak area ratio on a GPC chart of 4 - 30 %.

When the amount of the high molecular weight component is less than 4 %, the effect of improving the heat generation is not sufficient. On the contrary, when the content exceeds 30 %, the softening temperature of the resin becomes so high that the dispersion in a rubber becomes insufficient and the heat generation property is rather deteriorated.

The amount of the high molecular weight component is measured by the method as illustrated in FIG. 1.

FIG. 1 is a GPC chart where the abscissa represents the retention time (min.) while the ordinate represents the peak strength (MU). The sample is a solvent solution of a xyleneol-phenol, cresol-aldehyde copolycondensation resin according to the present invention.

The hatched area "A" is the area corresponding to the retention time range shorter than the retention time (10.97 min.) of the standard polystyrene sample A 5000 (molecular weight of 5200).

The total peak area is the sum of the "A" and the dotted area "B".

The ratio of A to (A + B) represents the peak area ratio of the high molecular weight component.

For purposes of improving remarkably each of characteristics of the rubber composition such as elasticity, breaking resistance and heat generation property, the resin is preferably a high ortho copolycondensed novolac resin having the ratio (o/p) of ortho bond (o) to para bond (p) of 2 or more.

The catalyst for preparing the high ortho copolycondensed novolac resin may be, for example, an organic acid salt, inorganic acid salt or oxide of divalent metal ion of alkaline earth metals, zinc, manganese, cadmium and the like, and preferably zinc acetate.

5 The amount of the copolycondensed novolac resin used is 0.5 - 10 parts by weight based on 100 parts by weight of the rubber.

When the amount of said resin is less than 0.5 parts by weight, elasticity is not sufficiently increased by the addition. When the amount of said resin exceeds 10 parts by weight, the increased amount over 10 parts by weight does not exhibit any good effect, and the breaking resistance and heat generation property are rather deteriorated.

10 According to the present invention, a compound capable of donating a methylene group when heated is incorporated in the composition so as to cure the above-mentioned copolycondensed novolac resin by forming a three dimensional network and impart a high elasticity to the rubber composition.

The compound capable of donating a methylene group when heated may be hexamethylenetetramine, polymethylolmelamine derivatives, oxazoline derivatives, and polymethylol-acetylene urea. Among them, 15 hexamethylenetetramine and polymethylol-melamine derivative are preferable. More particularly, polymethylol-melamine derivative is preferable which does not adversely affect the other members and working environment during heating.

20 The amount of this compound is 0.5 - 10 parts by weight based on 100 parts by weight of the rubber. When the amount is less than 0.5 parts by weight, the effect caused by the addition is not sufficient. On the contrary, when the amount exceeds 10 parts by weight, the incremental amount does not so improve the characteristics of the rubber composition.

25 In addition to the above-mentioned novolac resin, a compound capable of donating a methylene group when heated, and ordinary reinforcing agents such as carbon black, silica and the like, if necessary, there may be optionally incorporated into the rubber composition antioxidants, softeners, vulcanization accelerators, vulcanization accelerating auxiliaries, sulfur or adhesive promoters which are usually used in rubber industry.

As mentioned above, according to the present invention, the rubber composition has compatibly high elasticity and high breaking resistance.

30 In addition, the rubber composition has compatibly high elasticity, high breaking resistance, and an improved heat generation property. Further, the elongation upon breaking is also improved.

The rubber composition of the present invention is suitable for tires, conveyor belts, hoses and the like. Further, the rubber composition of the present invention can be effectively used at a portion which is subjected to a thermal oxidative deterioration and a mechanical repeated load, for example, a rubber composition covering steel cords of tires.

35 The present invention is now more particularly described with reference to the following examples which are for the purpose of illustration only and are intended to imply no limitation thereon.

Firstly there are explained the processes for preparing resins used. All parts and percentages are by weight in the following unless otherwise specified.

#### 40 Resin Preparation Example 1

3,5-Xylenol 366 parts, 41.5 % formalin 151.8 parts, and oxalic acid 0.73 parts were reacted at a temperature of the boiling point of the reaction mixture or higher under reflux for 3 hours. After completion of the reaction, the reaction fluid was heated up to 180°C at ordinary temperature while removing water, and further, unreacted xylenol was removed under reduced pressure to obtain 374 parts of novolac resin having a softening point (ring and ball method) of 100°C.

The resulting resin was analyzed using tetrahydrofuran as a solvent under the following conditions by means of a GPC apparatus to measure the content of the high molecular weight component.

45 GPC apparatus : Manufactured by Tohsoh Corp.

50 Column : Manufactured by Tohsoh Corp. TSK - GEL 2000, Two tubes

Solvent : Tetrahydrofuran (THF) 1cc/min.

Detector : RI

Standard polystyrene sample : Manufactured by Tohsoh Corp., A500, A1000, A2500, and A5000

55 There was measured the content of the high molecular weight component having a molecular weight of 5200 or more in terms of polystyrene (hereinafter referred to as "high molecular weight component") in the resin as a peak area ratio on the GPC chart according to the following procedure.

The time "10.97 min." in the GPC chart in FIG. 1 corresponding to the retention time of the standard polystyrene sample A5000 (molecular weight of 5200) is taken as a standard, and the content of the high

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molecular weight component is calculated by the following formula:

$$\text{Peak area ratio (\%)} = [A/(A + B)] \times 100$$

- 5 where A is a peak area corresponding to the retention time shorter than the standard, i.e. the region of molecular weight higher than the molecular weight corresponding the standard, and (A + B) is the total peak area.

As a result of the analysis, the content of the high molecular weight component of this resin was 1.0 %.

## 10 Resin Preparation Example 2

Phenol 188 parts, 41.5 % formalin 115.7 parts (hereinafter referred to as "primary formalin"), and oxalic acid 1.84 parts were mixed and reacted at a boiling temperature of the reaction system or higher under reflux for 15 min. and then quenched followed by keeping the reaction fluid at 60 - 70 °C for one hour.

- 15 Then, 3,5-xylenol 732 parts was added to the resulting reaction fluid and the temperature was raised, and the reaction was carried out under reflux for 2 hours while 41.5 % formalin 316.6 parts (hereinafter referred to as "secondary formalin") was gradually added thereto.

- 20 After completion of the reaction, the temperature was raised up to 180 °C while removing water at ordinary pressure and then the unreacted phenol, and xylenol were removed at a reduced pressure to obtain a copolycondensed novolac resin (916 parts) having a softening temperature (ring and ball method) of 116 °C and containing 5.2 % of high molecular weight component.

- 25 The reaction proportion of xylenol (A) to phenol (B) (hereinafter simply referred to as "reaction proportion" unless otherwise stated) was calculated from the amounts of xylenol and phenol fed and the amounts of unreacted xylenol and phenol recovered by distillation at a reduced pressure. The resulting molar ratio (A/B) was 27 : 73.

## Resin Preparation Example 3

- 30 The procedure of Resin Preparation Example 2 was repeated except that there were used phenol 282 parts, primary formalin 173.5 parts, oxalic acid 2.59 parts, 3,5-xylenol 366 parts, and secondary formalin 156.2 parts, and there was produced 634 parts of a copolycondensed novolac resin of reaction proportion of 54 : 46, having a softening temperature of 117 °C and containing 9.0 % of the high molecular weight component.

## 35 Resin Preparation Example 4

- 35 The procedure of Resin Preparation Example 2 was repeated except that there were used phenol 567 parts, primary formalin 347 parts, oxalic acid 3.23 parts, 3,5-xylenol 244 parts and secondary formalin 86.7 parts, and there was obtained a copolycondensed novolac resin (783 parts) of reaction proportion of 78 : 22, having a softening point of 110 °C and containing 9.0 % of the high molecular weight component.

## Resin Procurement Example 5

- 45 As a phenol novolac resin, there was used PLYOPHEN GH-6059 manufactured by DAINIPPON INK & CHEMICALS INC.

This resin had a softening point of 114 °C and contained 22.4 % of the high molecular weight component.

## 50 Resin Preparation Example 6

- 50 The procedure of Resin Preparation Example 2 was repeated except that phenol 282 parts, primary formalin 173.5 parts, oxalic acid 2.59 parts, 3,5-xylenol 366 parts, and secondary formalin 86.7 parts were used, and there was obtained a copolycondensed novolac resin (600 parts) of reaction proportion of 52 : 48, having a softening point of 80 °C and containing 2.0 % of the high molecular weight component.

Resin Preparation Example 7

5 The procedure of Resin Preparation Example 2 was repeated except that there were used phenol 282 parts, primary formalin 195.2 parts, oxalic acid 2.59 parts, 3,5-xylenol 366 parts and secondary formalin 216.9 parts, and there was obtained a copolycondensed novolac resin (662 parts) of reaction proportion of 54 : 46, having a softening point of 154 °C and containing 35.2 % of the high molecular weight component.

Resin Preparation Example 8

10 The procedure of Resin Preparation Example 2 was repeated except that phenol 282 parts, primary formalin 173.5 parts, oxalic acid 2.59 parts, 3,5-xylenol 366 parts, and secondary formalin 151.8 parts, and there was obtained a copolycondensed novolac resin (655 parts) of reaction proportion of 54 : 46, having a softening point of 138 °C and containing 26.4 % of the high molecular weight component.

15 Resin Preparation Example 9

20 The procedure of Resin Preparation Example 2 was repeated except that there were metha-cresol 324 parts, primary formalin 173.5 parts, oxalic acid 2.59 parts, 3,5-xylenol 366 parts, and secondary formalin 156.2 parts, there was obtained a copolycondensed novolac resin (673 parts) of reaction proportion of 51 : 49 [xylenol (A): cresol (B)], having a softening temperature of 138 °C and containing 3.0 % of the high molecular weight component.

Resin Preparation Example 10

25 Xylenol novolac resin of Resin Preparation Example 1 500 parts and phenol novolac resin of Resin Procurement Example 5 500 parts were heated to 180 °C to melt and mix, and there was obtained a mixture having a softening point of 106 °C and containing 15 % of the high molecular weight component.

Resin Preparation Example 11

30 Phenol 282 parts, 41.5 % formalin 173.5 parts, and zinc acetate 3.24 parts were reacted under reflux for 6 hours at a boiling point of the mixture or higher, then quenched and kept at 60 - 70 °C for one hour.

And then 3,5-xylenol 366 parts and 41.5 % formalin 111.4 parts were gradually added to the above-mentioned reaction mixture. While removing water at ordinary pressure, the resulting mixture was heated to 35 110 °C, and then reacted under reflux for 3 hours.

Further, while removing water at ordinary pressure, the mixture was heated to 120 °C and reacted under reflux for 3 hours again. Then, still further while removing water at ordinary pressure, the mixture was heated to 140 °C and reacted under reflux for 3 hours again.

After completion of the reaction, while removing water at ordinary pressure, the mixture was heated to 40 180 °C, and then unreacted phenol and xylenol were removed at reduced pressure, and there was obtained a high ortho copolycondensed resin (523 parts) of reaction proportion of 54 : 46, having a softening point (ring and ball method) of 120 °C and containing 1.0 % of the high molecular weight component.

The ratio (o/p) of ortho bond to para bond of the resulting resin was calculated from the ratio of peak strength of the remaining methine group of phenol nucleus to that of xylenol nucleus determined by means 45 of <sup>13</sup>C-NMR. As a result, the o/p ratio was 2.3.

Resin Preparation Example 12

50 p-t-Octylphenol 618 parts, primary formalin 173.5 parts, and oxalic acid 2.59 parts were reacted under reflux for 60 min. and further 3,5-xylenol 366 parts and secondary formalin 156.2 parts were used. Then the reaction was carried out in the same manner as in Resin Preparation Example 2 to produce a copolycondensed novolac resin (634 parts) having a softening point 132 °C and containing 7.5 % of the high molecular weight component.

55 EXAMPLES 1 - 6 and COMPARATIVE EXAMPLES 1 - 6

To 100 parts of a rubber prepared by blending 80 parts of natural rubber and 20 parts of synthetic polyisoprene rubber were added 55 parts of HAF carbon black, one part of aroma oil, 10 parts of zinc oxide,

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1.5 parts of Santoflex 13 (trade name, manufactured by Monsanto), 2.0 parts of cobalt naphthenate, 1.0 parts of N-tert-butyl-2-benzothiazolyl sulfenamide, and 5 parts of sulfur.

The resulting rubber composition was compounded with 1.5 parts of each of the resins in Tables 1 - 3 and the predetermined amount of hexamethoxymethylmelanine.

5 Each of the resulting 12 kinds of rubber compositions was formed into a sheet of 2 mm thick, which was then vulcanized at 145 °C for 40 min.

The dynamic modulus of elasticity ( $E'$ ,  $\tan \delta$ ) at room temperature of each of the sheets thus vulcanized was measured under conditions: initial load of 160 g; dynamic strain of 1 % and frequency 50 Hz by means of a viscoelastic meter manufactured by Iwamoto Seisakusho.

10 In addition, the tensile strength thereof was measured according to JIS K 6301 and the elongation upon breaking was also measured.

The results are shown in Tables 1, 2 and 3. Further in Table 1 are listed Conventional Example 1 where no resin was compounded, Conventional Example 2 where the amount of sulfur was increased up to 7 parts, and Conventional Example 3 where the amount of carbon black was increased up to 70 parts.

15 In Tables 1, 2 and 3 are listed Comparative Example 1 where xylene alone was used, Comparative Example 2 where phenolic resin alone was used, Comparative Example 3 where the softening point was too low, Comparative Example 4 where the softening point was too high, Comparative Example 5 where copolycondensation was not carried out, and Comparative Example 6 where neither phenol nor cresol was used.

20 The results are shown by an index assuming that the value of the result of Conventional Example 1 is 100. The larger the value, the better the result.

As is clear from the results in Tables 1, 2 and 3, the rubber compositions of the present invention shown in Examples can attain high compatibility of high elasticity and breaking resistance, and moreover have an excellent heat generation property.

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Table 1

Type of resin	Conventional Example 1		Conventional Example 2		Conventional Comparative Example 1 Example 3		Example 1		Example 2	
	None	Increased amount of sulfur	None	Increased amount of black carbon	Resin Preparation Example 1	Resin Preparation Example 2	Resin Preparation Example 1	Resin Preparation Example 2	Resin Preparation Example 3	Resin Preparation Example 3
Hexamethoxy-methylmaleimine (% by weight)					2.5	2.5	2.5	2.5	2.5	2.5
Result										
Dynamic modulus of elasticity ( $E'$ )	100	120	106	80	148	160	95	106	194	197
$\tan \delta$	100	106	86	68					107	110
Elongation upon breaking	100	86	68	68				106	104	105

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Table 2

Type of resin	Example 3	Comparative Example 2	Comparative Example 3	Comparative Example 4	Example 4	Example 5
	Resin Preparation Example 4	Resin Preparation Example 5	Resin Preparation Example 6	Resin Preparation Example 7	Resin Preparation Example 8	Resin Preparation Example 9
Hexamethoxy-methylmethacrylate (% by weight)	2.5	2.5	2.5	2.5	2.5	2.5
Result						
Dynamic modulus of elasticity (E')	165	135	152	147	203	176
<u><math>\tan \delta</math></u>	110	100	98	92	115	106
Elongation upon breaking	103	101	106	97	102	103

Table 3

	<u>Comparative Example 5</u>	<u>Example 6</u>	<u>Comparative Example 6</u>
<u>Type of resin</u>	<u>Resin Preparation Example 10</u>	<u>Resin Preparation Example 11</u>	<u>Resin Preparation Example 12</u>
<u>Hexamethoxy-methylmelamine (% by weight)</u>	2.5	2.5	2.5
<u>Result Dynamic modulus of elasticity (E')</u>	151	210	120
<u><math>\tan \delta</math></u>	100	115	90
<u>Elongation upon breaking</u>	103	104	103

EXAMPLES 7 - 10, COMPARATIVE EXAMPLES 7 - 10

One hundred parts of a rubber prepared by blending 50 parts of natural rubber and 50 parts of styrene-butadiene copolymer rubber was mixed with 40 parts of ISAF carbon black, 2 parts of stearic acid, 13.40 parts of Santoflex, 3 parts of zinc oxide, 1.0 parts of N-tert-butyl-2-benzothiazolylsulfenamide and 1.5 parts of sulfur. The resulting rubber composition was compounded with various amounts of resins of Resin Preparation Examples 1 - 5 and hexamethoxymethylmelamine, and evaluation was effected in a way similar to Example 1.

The results are shown in Table 4. For comparison, there are also shown in Table 4 Conventional Example 4 where neither resin nor melamine was compounded and Conventional Example 5 where the amount of carbon black was increased up to 50 parts.

The results are shown by an index assuming that the value of the result of Conventional Example 4 is 100. The larger the value, the better the result. In Comparative Example 7 there was used a xylanol resin alone and in Comparative Example 8 there was used a phenolic resin alone.

Neither the amount of hexamethoxymethylmelamine in Comparative Example 9 nor the amount of the resin in Comparative Example 10 is within the range of the present invention.

As is clear from the results in Table 4, the rubber compositions of the present invention shown in Examples can attain high compatibility of high elasticity and breaking resistance, and moreover have an excellent heat generation property.

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Table 4

	Resin used (Parts by weight)	Hexamethoxy- methylmetha- mine (Parts by weight)	Dynamic modulus of elasticity (E')	$\tan \delta$	Elongation upon breaking
Conventional Example 4	None	—	100	100	100
Conventional Example 5	Increased amount of carbon black	—	126	85	78
Comparative Example 7	Resin Preparation Example 1 (8.0)	5.0	173	102	91
Example 7	Resin Preparation Example 2 (8.0)	5.0	210	104	97
Example 8	Resin Preparation Example 3 (4.0)	2.5	192	107	100
Example 9	Resin Preparation Example 3 (8.0)	5.0	227	103	98
Example 10	Resin Preparation Example 4 (8.0)	5.0	204	103	98
Comparative Example 8	Resin Preparation Example 5 (8.0)	5.0	153	101	92
Comparative Example 9	Resin Preparation Example 3 (2.5)	0.25	113	104	108
Example 11	Resin Preparation Example 3 (2.5)	0.75	149	105	105
Example 12	Resin Preparation Example 3 (8.0)	9.5	238	98	96

Table 4 (cont'd)

	Resin used (Parts by weight)	Hexamethoxy- methylmethane (Parts by weight)	Dynamic modulus of elasticity (E')	$\tan \delta$	Elongation upon breaking
Comparative Example 10	Resin Preparation Example 3 (0.25)	2.5	138	97	103
Example 13	Resin Preparation Example 3 (0.75)	2.5	160	105	102
Example 14	Resin Preparation Example 3 (9.5)	7.5	235	100	97

## Claims

1. A rubber composition which comprises 100 parts by weight of a rubber selected from the group consisting of natural rubber, synthetic rubber and a mixture thereof, 0.5 - 10 parts by weight of a novolac resin having a softening point of 90 - 150 °C prepared by the copolycondensation of xylolol (A) and a phenol (B) selected from the group consisting phenol, cresol and a mixture thereof at a molar ratio (A/B) ranging from 25/75 to 75/25, by using an aldehyde compound, and 0.5 - 10 parts by weight of a compound capable of donating a methylene group when heated.

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2. The rubber composition according to claim 1 in which the xlenol (A) is 3,5-xlenol.
3. The rubber composition according to claim 1 in which the molar ratio of xlenol (A) to a phenol (B) ranges from 40/60 to 60/40.
5. The rubber composition according to claim 1 in which the copolycondensed novolac resin contains a high molecular weight component having a molecular weight in terms of polystyrene of 5200 or more in an amount corresponding to a peak area ratio on a GPC chart of 4 - 30 %.
10. 5. The rubber composition according to claim 1 in which the copolycondensed novolac resin prepared from xlenol (A) and a phenol (B) is a high-ortho copolycondensed novolac resin having a ratio (o/p) of ortho bond to para bond of 2 or more.
15. 6. The rubber composition according to claim 1 in which the compound capable of donating a methylene group is at least one member selected from the group consisting of hexamethylenetetramine, polymethylol-melamine derivatives, oxazoline derivatives, and polymethylol-acetylene urea.

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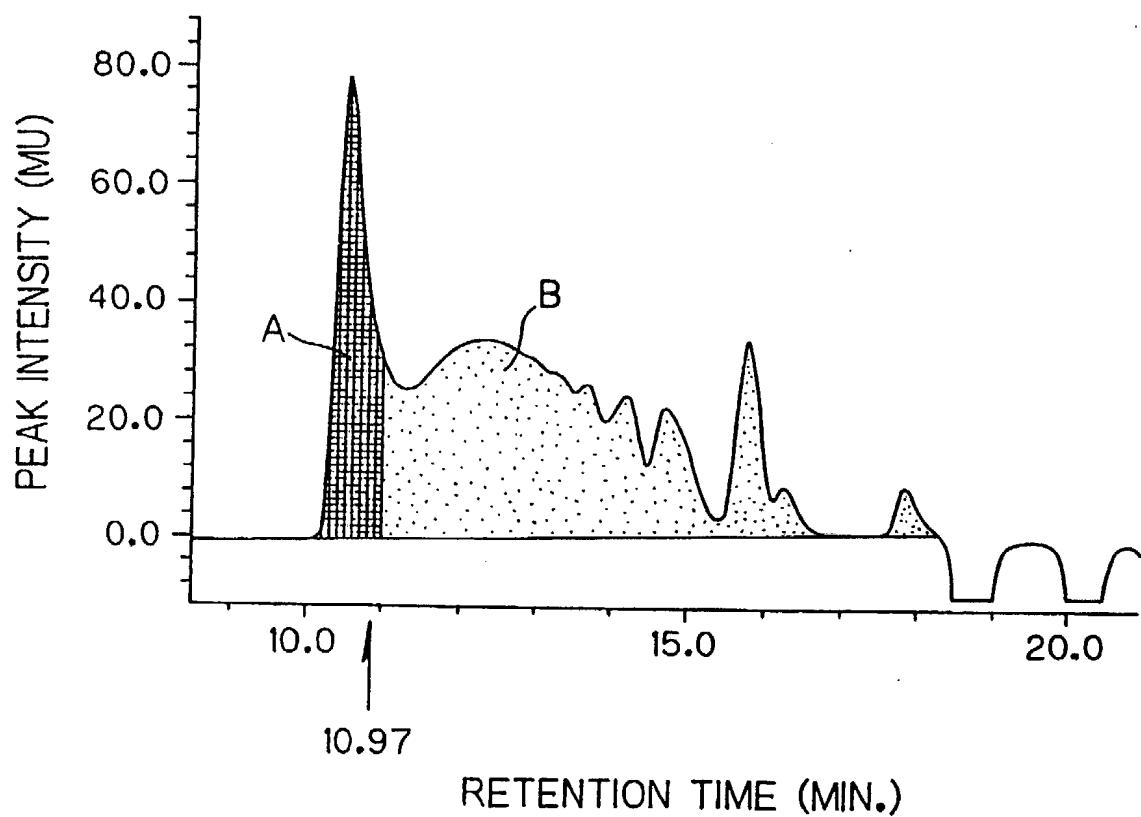
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FIG. 1





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 12 0767

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. CL.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 281 (C-200)(1426) 15 December 1983 & JP-A-58 160 331 ( SUMITOMO KAGAKU KOGYO K.K. ) 22 September 1983 * abstract * --- A EP-A-0 197 395 (HOECHST AG) * claim 1 * --- A DATABASE WPIL Section Ch, Week 2991, Derwent Publications Ltd., London, GB; Class A, AN 91-213490 & SU-A-590 966 (SHEPELEVA I.P.) 28 February 1991 * abstract * -----	1 1 1	C08L21/00 //(C08L21/00, 61: 04)
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C08L
<p>The present search report has been drawn up for all claims</p>			
Place of search <b>THE HAGUE</b>	Date of completion of the search <b>25 MARCH 1993</b>	Examiner <b>VAN HUMBEECK F.</b>	
<b>CATEGORY OF CITED DOCUMENTS</b>		<b>T : theory or principle underlying the invention</b> <b>E : earlier patent document, but published on, or</b> <b>after the filing date</b> <b>D : document cited in the application</b> <b>L : document cited for other reasons</b> ----- <b>A : member of the same patent family, corresponding</b> <b>document</b>	
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